3-53

THE GRADUATE SCHOOL

University of Florida

REPORT ON THESIS OR DISSERTATION AND/OR FINAL EXAMINATION

TO THE DEAN OF THE GRADUATE SCHOOL:

Mr. Wesley Lamar Miller has submitted,

in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in the College of

Arts and Sciences, a thesis entitled

Preparation of Stereospecific Polymers Through A Cyclic Polymerization Mechanism

This thesis has been examined by all members of the candidate's special supervisory committee and has been approved ~~XXXXXX~~ (delete one). The committee has examined the candidate in accordance with the regulations governing the Final Examination and has adjudged his performance satisfactory ~~unsatisfactory~~ (delete one). Exceptions or qualifications are noted as follows:

SUPERVISORY COMMITTEE:

Date October 28, 1960

G B Butler	G. B. Butler *Chairman*	Chemistry
W. T. Lippincott	W. T. Lippincott	"
W S Brey	W. S. Brey, Jr.	"
A H Gropp	A. H. Gropp	"
	Paul M. Downey	Industrial Eng.

Approved:

Asst J E Hawkins
Department Head

A H Gropp
Dean of the College

Dean of the Graduate School

DIRECTIONS: Two copies of this form are signed by all members of the special supervisory committee and by the Dean of the College or his representative, and one copy thus signed is sent to the Dean of the Graduate School.

PREPARATION OF STEREOSPECIFIC POLYMERS THROUGH A CYCLIC POLYMERIZATION MECHANISM

By

W. LAMAR MILLER

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
January, 1961

ACKNOWLEDGMENTS

In the undertaking of a task such as the recording of information gained over a long period of time on any given subject, it would not be possible for the author to say how he acquired any given body of knowledge. If such be the case, then it must be admitted that this work is not entirely the work of an individual but rather is the work of many people. It is only possible to record what many have taught to an individual student.

Since it is impossible for the author to acknowledge his thanks to all of these people, then he must be limited to those who aided directly in the completion of this work.

The author would like to express his deep gratitude to his research director, Dr. George B. Butler, for his patience, encouragement, and capable direction of this work. The author is also indebted to Drs. W. S. Brey, Jr. and H. G. Clark, III, for many enlightening discussions and help at times when it was most needed. The author also wishes to thank his supervisory committee for many valuable suggestions and encouragement. To Mrs. Marie Eckart for typing the manuscript goes a special expression of thanks.

The author is also indebted to the Chemstrand Corporation for their support of this work by providing The Chemstrand Fellowship for Research in High Polymers during the year 1959-1960.

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS ii

LIST OF TABLES vi

LIST OF ILLUSTRATIONS vii

CHAPTER

I. INTRODUCTION 1

II. PREPARATION AND CHARACTERIZATION OF N,N-DIALLYLAMIDES . . 2

- A. Nomenclature 3
- B. Materials 3
- C. Physical Measurements 3
- D. Preparations 5
  - 1. N,N-Diallylformamide 5
  - 2. N,N-Diallylacetamide 5
  - 3. N,N-Diallyl-trifluoroacetamide 6
  - 4. N,N-Diallylpropionamide 6
  - 5. N,N-Diallylheptanamide 7
  - 6. N,N-Diallylnonanamide 8
  - 7. N,N-Diallyl-N-tricyanovinylamine 8

III. POLYMERIZATION STUDIES ON DIALLYLAMIDES 14

- A. Materials 15
- B. Polymerization Procedure 15
- C. Homopolymerization Attempts 16
- D. Telomerization Reactions 19

TABLE OF CONTENTS (continued)

Page

1. Addition of Ethyl Bromoacetate to Diallylacetamide and Diallylpropionamide . 19
    a. Diallylacetamide 19
    b. Diallylpropionamide 20
2. Addition of Bromotrichloromethane to Diallylacetamide and Diallylpropionamide . 20
    a. Diallylacetamide 20
    b. Diallylpropionamide 20
3. Attempted Separation of Adducts 21

IV. INFRARED INVESTIGATION OF THE DIALLYLAMIDES AND RELATED COMPOUNDS 23

V. STUDIES ON POLY-(METHACRYLIC ANHYDRIDE) 29

A. Materials 31
B. Polymerization Procedure 32
C. Hydrolysis to Poly-(Methacrylic Anhydride) 33
    1. General Method of Hydrolysis 33
    2. Basic Hydrolysis 36
    3. Mild Hydrolysis 36
D. Esterification of Poly-(Methacrylic Acid) 37
E. X-Ray Diffraction Studies 39
F. Nuclear Magnetic Resonance Studies 40
    1. Preparation of NMR Samples 44
    2. Measurements 45

TABLE OF CONTENTS (continued)

Page

G. Interpretation of Results 45

VI. SUMMARY 51

BIBLIOGRAPHY 53

BIOGRAPHICAL NOTES 56

LIST OF TABLES

Table Page

I. PROPERTIES OF THE COMPOUNDS PREPARED 10

II. ANALYSIS OF THE COMPOUNDS PREPARED 12

III. ATTEMPTED POLYMERIZATION OF DIALLYLAMIDES 17

IV. ABSORPTION FREQUENCY OF IN-PLANE-DEFORMATION VIBRATION OF TERMINAL METHYLENE GROUP. 26

V. RESULTS OF METHACRYLIC ANHYDRIDE POLYMERIZATIONS 34

VI. HYDROLYSIS OF POLY-(METHACRYLIC ANHYDRIDE) TO POLY-(METHACRYLIC ACID). 35

VII. CONVERSION OF POLY-(METHACRYLIC ACID) TO POLY-(METHYL METHACRYLATE) BY REACTION WITH DIAZOMETHANE 38

VIII. FRACTIONS OF POLY-(METHYL METHACRYLATE) IN THE THREE STEREO CONFIGURATIONS AS DETERMINED BY NMR 46

LIST OF ILLUSTRATIONS

Figure | Page

1. The probabilities of occurrence of isotactic, P_i, heterotactic, P_h, and syndiotactic, P_s, sequences of monomer units as a function of α, the probability of isotactic placement of monomer units during propagation 43
2. The probabilities of occurrence of isotactic, heterotactic and syndiotactic sequences of monomer units as a function of α, the probability of isotactic placement of monomer units during propagation. The fraction of isotactic is placed on the isotactic line to determine the value of α. 47
3. Plot of log of the percentage of isotactic fraction in the poly-(methyl methacrylate) samples versus the temperature of polymerization . . . 49

CHAPTER I

INTRODUCTION

Previous work in both these[1-7] and other[8-18] laboratories has conclusively demonstrated that many non-conjugated diene systems may be polymerized to linear, soluble polymers containing a recurring cyclic unit. Reports[2,3] from these laboratories have outlined a mechanism for these systems and offered evidence to prove the presence of the recurring cyclic units in the polymers.

The original work on this type of polymer system was the free radical polymerization of diallyl quaternary ammonium salts. The intramolecular—intermolecular chain propagation mechanism has since been extended to cover diene systems initiated by free radical initiators,[1-10] cationic,[18] and anionic[16,18] initiators, and Ziegler-type initiating systems.[7,11,12,13,18] The monomers have been extended to cover systems such as 1,5 and 1,7 dienes of many structural types as well as higher α,α'-olefin systems.[11,13]

The main objectives in this investigation were as follows: 1) To investigate monomer systems which may give evidence to explain why these diene systems undergo the cyclic polymerization mechanism. 2) To investigate one polymerization system to determine whether any stereo-control is exerted via this mechanism. 3) To determine what effect the stereo-control will have on the configuration of the polymers produced via this mechanism.

CHAPTER II

PREPARATION AND CHARACTERIZATION OF N,N-DIALLYLAMIDES

Since work in these laboratories has shown that diallyldimethylammonium bromide and related quaternary ammonium salts could be polymerized quite readily while diallylamine did not polymerize under similar free radical conditions, it was decided to investigate the relation between monomer structure and polymerizability.

Other workers in these laboratories synthesized and polymerized diallylalkylphosphine oxides,[6] diallyldialkylphosphonium bromides,[7] and diallyldialkyl silanes,[7] but these compounds are dissimilar from the series under consideration in that they contain no central nitrogen atom.

With the exception of diallylformamide[19] and diallylacetamide,[20] no reference is made to the diallyl amides in the literature. No data were given in the single references to diallylformamide and diallylacetamide to their preparation and properties. The preparations in this work follow the general methods outlined by Hickinbottom.[21]

The inclusion of diallyltricyanovinylamine in this section seemed reasonable since the effect of the substituents on the central nitrogen atom followed the same course as that of the amides.

A. Nomenclature

All nomenclature in this work will follow that used by *Chemical Abstracts*.

B. Materials

Formic acid and propionic anhydride were practical grade, purchased from Matheson, Coleman and Bell; thionyl chloride, quinoline, and heptanoic acid were purchased from Fisher Scientific Company. Nonanoic acid was practical grade, purchased from Rohm and Haas Company; acetic anhydride was purchased from Union Carbide Chemicals Company. Diallylamine was provided by the Shell Chemical Company, and tetracyanoethylene was graciously provided by Dr. V. A. Engelhardt, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Incorporated. Ethyl trifluoroacetate was furnished by W. S. Durrell, Department of Chemistry, University of Florida.

C. Physical Measurements

The crude reaction mixtures from the preparation of the amides were fractionally distilled to give 55-85% yields of a reasonably pure material. Prior to determination of the physical constants, the amides were all redistilled and a narrow cut consisting of about the middle one-third of the products taken for the determination of the physical constants. A gas chromatographic analysis indicated the presence of a single component in each sample used for the measurement of the physical properties. The gas chromatographic analyses were made on an Aerograph Gas Chromatographic Instrument using helium as the carrier gas and a five foot Aerograph 150-A-1 column (silicone on fire brick).

Distillation pressures were read on a Zimmerli gauge; temperatures are °C. and are uncorrected.

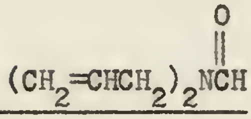
The refractive indexes were measured by means of a Bausch and Lomb Abbe 3L refractometer fitted with an achromatic compensating prism.

Densities were determined on approximately five milliliter samples, and all weighings were made on an analytical balance.

The heats of vaporization were calculated from at least four different temperatures and pressures using the Clausius-Clapeyron equation. These should be considered as approximate values only.

The elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

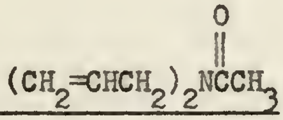
D. Preparation



1. N,N-Diallylformamide, $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}H$

Formic acid (25 g., 0.54 mole) was added dropwise with stirring to diallylamine (50 g., 0.52 mole) and the reaction was allowed to stir for one hour. The mixture was then heated to remove excess reactants and the water formed during the reaction. The temperature was maintained at 150° for one hour and the residue distilled off at reduced pressure. The crude product was redistilled and a careful fractionation gave a clear, water-white liquid (48.9 g., 65.2%), b.p. 81.5° at 9.0 mm., 88.2° at 12.4 mm., 93.0° at 15.8 mm., 96.5° at 19.0 mm.; $n_D^{21.5}$ 1.4693; $d^{21.5}$ 0.9326. MR_D 37.395, calcd. 37.413; ΔH_v 13,200 ± 1,000 cal. mole^{-1} deg.$^{-1}$; retention time, 4.12 minutes at 196°, helium flow rate, 20 ml./min.

Anal. Calcd. for $C_7H_{11}NO$: %C, 67.17; %H, 8.86; %N, 11.19.
Found: %C, 67.34; %H, 9.03; %N, 11.04.



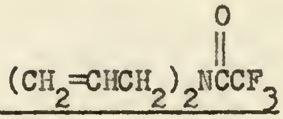
2. N,N-Diallylacetamide, $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}CH_3$

Diallylamine (49 g., 0.5 mole) was added dropwise with stirring to acetic anhydride (51 g., 0.5 mole); the mixture was then refluxed gently for twenty-four hours. Unreacted materials and acetic acid were removed by distillation at atmospheric pressure, and the remaining crude product was distilled at reduced pressures. Fractionation gave a clear, water-white liquid (60.0 g., 85.7%), b.p. 95° at 12.7 mm., 98° at 14.6 mm., 100° at 16.3 mm., 101.4° at 17.3 mm., 103.2° at 19.0 mm.;

n_D^{21} 1.4693; d^{21} 0.9341. MR_D 41.516, calcd. 42.031; ΔH_v 13,500 ± 1,500 cal. $mole^{-1}$ $deg.^{-1}$; retention time, 4.96 minutes at 200°, helium flow rate, 20 ml./min.

Anal. Calcd. for $C_8H_{13}NO$: %C, 69.03; %H, 9.41; %N, 10.07.
Found: %C, 68.85; %H, 9.64; %N, 10.21.

3. N,N-Diallyl-trifluoroacetamide,

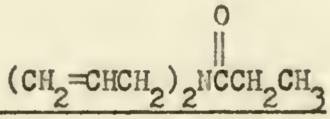


$$(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}CF_3$$

Diallylamine (50 g., 0.52 mole) was added dropwise to ethyl trifluoroacetate (75 g., 0.53 mole). The reaction mixture was protected by a Drierite tube and allowed to stand at room temperature for one week. The reaction mixture was fractionally distilled to yield a clear, water-white liquid (80.0 g., 80.5%), with a pungent, nauseating odor, b.p. 71.3° at 15.3 mm., 76.5° at 20 mm., 81.1° at 25 mm., 84.3° at 30 mm.; $n_D^{20.5}$ 1.4130; $d^{20.5}$ 1.138. MR_D 42.342, calcd. 42.031; ΔH_v 12,800 ± 1,500 cal. $mole^{-1}$ $deg.^{-1}$; retention time, 2.65 minutes at 195°, helium flow rate, 20 ml./min.

Anal. Calcd. for $C_8H_{10}NOF_3$: %C, 49.74; %H, 5.22; %N, 7.25.
Found: %C, 50.01; %H, 5.21; %N, 7.03.

4. N,N-Diallylpropionamide,



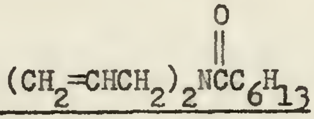
$$(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}CH_2CH_3$$

Diallylamine (44 g., 0.045 mole) was added dropwise with stirring to propionic anhydride (59 g., 0.45 mole) over a one hour period. The mixture was heated to reflux and maintained at reflux for sixteen hours with stirring. On careful fractionation, the reaction mixture yielded a clear, water-white liquid (50.2 g., 80%), diallylpropionamide,

b.p. 110-111° at 20 mm. Refractionation gave b.p. 86.0° at 5.6 mm., 96.0° at 9.5 mm., 102.0° at 12.6 mm., 110° at 19 mm.; n_D^{24} 1.4685; d^{24} 0.9203. MR_D 46.326, calcd. 46.649; ΔH_v 13,600 ± 300 cal. $mole^{-1}$ $deg.^{-1}$; retention time, 6.30 minutes at 200°, helium rate, 20 ml./min.

Anal. Calcd. for $C_9H_{15}NO$: %C, 70.55; %H, 9.87; %N, 9.14.

Found: %C, 70.61; %H, 9.89; %N, 9.32.

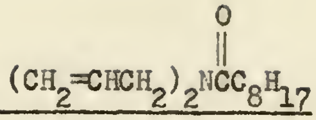


5. N,N-Diallylheptanamide, $(CH_2{=}CHCH_2)_2N\overset{O}{\overset{\|}{C}}C_6H_{13}$

Heptanoyl chloride (30 g., 0.20 mole), prepared by the method outlined by Shirley[22] by reaction of thionyl chloride and heptanoic acid, was added dropwise with stirring to diallylamine (40 g., 0.41 mole) in benzene (100 ml.) over a one hour period. After addition was complete, the reaction mixture was heated to reflux and stirred for an additional four hours. The solid, amine hydrochloride, was removed by filtration, washed with 30 ml. of benzene, and discarded. The filtrates were combined; the benzene removed under reduced pressure; and the remaining crude product fractionally distilled to yield a clear, water-white liquid (29.3 g., 70%), diallylheptanamide, b.p. 143-144.5° at 9.6 mm. Refractionation gave b.p. 140° at 10 mm., 145° at 12.4 mm., 150° at 15.6 mm., 154° at 18.4 mm.; n_D^{22} 1.4672; d^{21} 0.8977; MR_D 64.706, calcd. 65.121; ΔH_v 15,300 ± 500 cal. $mole^{-1}$ $deg.^{-1}$; retention time, 8.45 minutes at 200°, helium flow rate, 70 ml./min.; 9.06 minutes at 227°, helium flow rate, 20 ml./min.

Anal. Calcd. for $C_{13}H_{23}NO$: %C, 74.59; %H, 11.08; %N, 6.69.

Found: %C, 74.66; %H, 11.11; %N, 6.72.



6. N,N-Diallylnonanamide, $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}C_8H_{17}$

Nonanoyl chloride (40 g., 0.28 mole), prepared by the same method as heptanoyl chloride above, was added dropwise with stirring to a benzene solution (100 ml.) of diallylamine (63 g., 0.65 mole) over a one hour period. After addition was completed, the reaction mixture was heated to reflux and stirred for an additional four hour period. The solid diallylamine hydrochloride was filtered off, washed with 30 ml. of benzene and discarded. The two benzene portions were combined, and the benzene was removed under reduced pressure. The remaining crude material was fractionally distilled to yield a clear, water-white liquid (37 g., 55.4%), diallylnonanamide, b.p. 101-102° at 0.5 mm. Refractionation gave b.p. 137° at 7.8 mm., 144° at 10.0 mm., 151.5° at 15.1 mm., 159.5° at 20.4 mm.; n_D^{21} 1.4664; d^{21} 0.8860; MR_D 74.274, calcd. 74.357; ΔH_v 13,700 $\pm$ 1,700 cal. mole^{-1} deg.$^{-1}$; retention time, 10.30 minutes at 200°, helium flow rate, 20 ml./min.

Anal. Calcd. for $C_{15}H_{27}NO$: %C, 75.89; %H, 11.47; %N, 5.90.
Found: %C, 75.89; %H, 11.33; %N, 5.96.

7. N,N-Diallyl-N-tricyanovinylamine

The general procedure used was as outlined by McKusick, *et al.*[23] for preparation of N,N-dialkyl-N-tricyanovinylamines. Diallylamine (7.6 g., 0.0785 mole) was added dropwise with stirring to tetracyanoethylene (10 g., 0.0780 mole) dissolved in tetrahydrofuran (200 ml.). The addition rate was adjusted so that the temperature of the reaction mixture did not rise above 35°. After addition was completed, the mixture was heated to reflux for a three hour period. The solvent was removed under reduced pressure to yield a black, viscous oil, soluble in acetone and ethanol, slightly soluble in benzene and insoluble in water and pentane. All attempts to crystallize this material were unsuccessful. The crude reaction mixture was degassed at less than 0.1 mm. for twenty-four hours. An attempt to sublime the product out of the crude mixture at 0.05 mm. and 90° was unsuccessful. A five gram sample was deposited from a warm, saturated, benzene solution onto a chromatographic column prepared from benzene and activated alumina. Elution with 200 ml. of benzene gave a clear, yellow solution. Attempts to precipitate a solid from the benzene solution by addition of non-solvents or by cooling were unsuccessful. Evaporation of the benzene under reduced pressure yielded a yellow-red oil. The product was identified as diallyltricyanovinylamine by infrared, ultraviolet and elemental analyses. An ethanol solution was used to determine the ultraviolet absorption spectrum: λ max. 3340 Å; ϵ 14,300.

Anal. Calcd. $C_{11}H_{10}N_4$: %C, 66.65; %H, 5.09; %N, 28.27.

Found: %C, 66.90; %H, 5.38; %N, 27.94.

TABLE I

PROPERTIES OF THE COMPOUNDS PREPARED

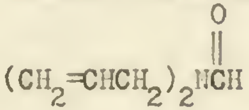
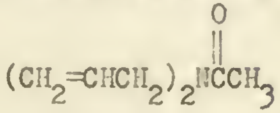
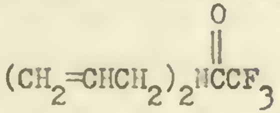
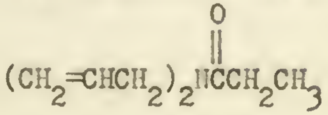
Compound	% Conversion	B.P. [°C./mm.Hg]	N_D^t	d^t	Retention Time V.P.C. [min./°C./ flow rate]	Heat of Vaporization [K cal./ mole-deg.]
Diallylformamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\Vert}}{C}H$	65.2	96.5/19.0	$1.4693^{21.5°}$	$0.9326^{21.5°}$	4.12/155/20	13.2 ± 1
Diallylacetamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\Vert}}{C}CH_3$	85.7	100 /16.3	$1.4693^{21°}$	$0.9341^{21°}$	4.96/200/20	13.5 ± 1.5
Diallyl-trifluoroacetamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\Vert}}{C}CF_3$	80.5	81.1/25	$1.4130^{20.5°}$	$1.138^{20.5°}$	2.65/195/20	12.8 ± 1.5
Diallylpropionamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\Vert}}{C}CH_2CH_3$	80.0	102.0/12.6	$1.4685^{24°}$	$0.9203^{24°}$	6.30/200/20	13.6 ± 0.3

TABLE I (continued)

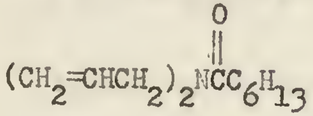
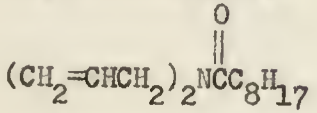
Compound	% Conversion	B.P. [°C./mm. Hg]	N_D^t	d^t	Retention Time V.P.C. [min./°C./ flow rate]	Heat of Vaporization [K cal./ mole-deg.]
Diallylheptanamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}C_6H_{13}$	70.0	140.0/10.0	$1.4672^{22°}$	$0.8977^{21°}$	8.45/200/70	15.3 ± 0.5
Diallylnonanamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}C_8H_{17}$	55.4	144.0/10.0	$1.4664^{21°}$	$0.8860^{21°}$	10.30/200/20	13.7 ± 1.7

TABLE II

ANALYSIS OF THE COMPOUNDS PREPARED

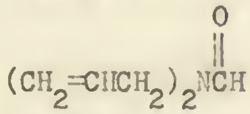
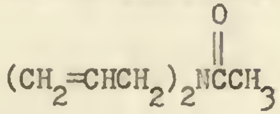
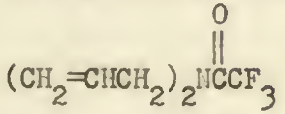
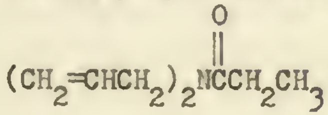
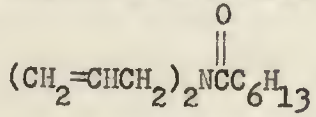
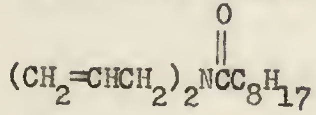
Compound	MR_D		% Carbon		% Hydrogen		% Nitrogen		% Oxygen[a]	
	[Calcd]	[Found]	[Calcd]	[Found]	[Calcd]	[Found]	[Calcd]	[Found]	[Calcd]	[Found]
Diallylformamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\parallel}}{C}H$	37.413	37.395	67.17	67.34	8.86	9.03	11.19	11.04	12.78	12.59
Diallylacetamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\parallel}}{C}CH_3$	42.031	41.516	69.03	68.85	9.41	9.64	10.07	10.21	11.50	11.30
Diallyl-trifluoroacetamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\parallel}}{C}CF_3$	42.031	42.342	49.74	50.01	5.22	5.21	7.25	7.03	—	—
Diallylpropionamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\parallel}}{C}CH_2CH_3$	46.649	46.326	70.55	70.61	9.87	9.89	9.14	9.32	10.44	10.18

TABLE II (continued)

Compound	MR_D		% Carbon		% Hydrogen		% Nitrogen		% Oxygen[a]	
	[Calcd]	[Found]	[Calcd]	[Found]	[Calcd]	[Found]	[Calcd]	[Found]	[Calcd]	[Found]
Diallylheptanamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}C_6H_{13}$	65.121	64.706	74.59	74.66	11.08	11.11	6.69	6.72	7.64	7.94
Diallylnonanamide,  $(CH_2{=}CHCH_2)_2N\overset{\overset{O}{\|}}{C}C_8H_{17}$	74.357	74.274	75.89	75.89	11.47	11.33	5.90	5.96	6.74	6.82
Diallyl-tricyanovinylamine, $(CH_2{=}CHCH_2)_2NC(CN){=}C(CN)_2$	—	—	66.65	66.90	5.09	5.38	28.27	27.94	—	—

a. % Oxygen calculated by difference

CHAPTER III

POLYMERIZATION STUDIES ON DIALLYLAMIDES

It was expected that the amides described above would undergo homopolymerization via the cyclic polymerization mechanism with varying degrees of success. This was expected because of the observations, pointed out earlier, that the diallyl quaternary ammonium halides did undergo cyclic polymerization while diallylamine did not. Also, other compounds such as the diallylphosphorus compounds,[6,7] mentioned earlier, and diallylphthalate[8,24-26] have been polymerized to soluble polymers by free radical initiators.

Several other workers have described soluble copolymers from diallyl systems, such as diallyl alkylamine oxides and acrylonitrile,[27] and a variety of other copolymer systems.[27,28]

The results obtained from attempts to polymerize the amides under a variety of conditions are given in this section. The monomers all contain the diallylamine unit with various substituents on the nitrogen atom.

Friedlander[29] has described the preparation of substituted tetrahydropyrans and tetrahydrothiopyrans via a cyclic reaction of allyl ether and allyl sulfide with chain transfer reagents, such as bromotrichloromethane, under free radical conditions. This line of approach was tried with the diallylamides in an attempt to prepare cyclic telomers. The results of these studies are also included in this section.

A. Materials

The preparations of the amides and tricyanovinylamine used in this study were described in a previous section of this work. Heptane, methanol, and xylene were from stock; benzene was stock, reagent grade, and was dried over sodium ribbon before use. The other chemicals were purchased: benzoyl peroxide and tert-butyl hydroperoxide from the Lucidol Division, Wallace and Tiernan, Incorporated; α,α-diazoisobutyronitrile from Eastman Organic Chemicals; bromotrichloromethane from the Dow Chemical Company; and ethyl bromoacetate from the Fisher Scientific Company.

B. Polymerization Procedure

Weighed quantities of the reactants, and solvent if used, in 20 ml. ampoules were flushed with dry nitrogen gas, and the ampoules were cooled in a Dry-Ice-acetone mixture before sealing off by use of an oxygen-methane torch. Polymerizations were carried out in an oven at the temperature and for the period of time indicated in Table III. This procedure was followed in all of the polymerization attempts except those in which the initiator was tert-butylhydroperoxide. In these experiments the samples were contained in a 100 ml. tube fitted with a reflux condenser and with a standard taper ground glass joint suitable for fitting into a refluxing xylene bath. In this way a constant temperature of 140° was maintained during these runs.

The polymers were isolated by addition of the reaction mixture to a large excess of methanol. The methanol mixtures were then filtered through a medium porosity sintered glass filter. The filters were dried *in vacuo* for twenty-four hours and the increase in weight taken as the yield of polymer in each case.

C. Homopolymerization Attempts

The conversions for the diallylamides, along with the conditions employed for each polymerization attempt are shown in Table III. The conversions are approximate values only but may be taken as indicative of the polymerizability of the monomers in a homopolymerization system. A blank in the table indicates less than 0.2% conversion and "trace" indicates conversions of 0.2-0.5%. The only samples which resulted in appreciable conversions were the tricyanovinyl and trifluoroacetyl derivatives. These two groups are also the two most electron withdrawing groups in the series. Since trace quantities of polymer were obtained from the formyl derivative, the next most powerful electron withdrawing substituent, there seems to be a definite correlation between the electron withdrawing power of the substituent on the nitrogen atom of diallylamine and the polymerizability of the monomer. Thus, it is observed that the stronger the electron withdrawing power of a substituent the more readily the monomer undergoes homopolymerization in a free radical system.

TABLE III

ATTEMPTED POLYMERIZATION OF DIALLYLAMIDES

Monomer	Monomer [g.]	Initiator [Type]	Initiator [Wt. % of Monomer]	Solvent	Temp. [°C.]	Time [hr.]	Conversion [*ca.* %]
Diallylformamide	0.93	BP[a]	3.0	benzene (50%)	85	95	trace
	0.93	BP	3.0	—	85	95	trace
	2.0	TBHP[b]	0.5	—	80	144	trace
	2.0	BP	1.0	—	80	144	trace
	2.0	ABN[c]	1.0	—	80	336	trace
Diallylacetamide	0.93	BP	3.0	benzene (50%)	85	95	—
	0.93	BP	3.0	—	85	95	trace
Diallyl-trifluoroacetamide	1.14	BP	3.0	benzene (50%)	85	95	3.5
	1.14	BP	3.0	—	85	95	6.4
	2.28	BP	1.1	—	80	49	3.0
	2.28	ABN	1.1	—	80	49	3.0
	2.85	ABN	3.0	—	73	25	5.0
Diallylpropionamide	1.11	BP	2.5	benzene (50%)	85	95	—
	1.11	BP	2.5	—	85	95	—
	5.0	TBHP	1.0	xylene (91%)	140	31	—
	6.0	TBHP	0.8	—	140	24	—
	10.0	TBHP	5.0	xylene (80%)	140	48	—
Diallylheptanamide	0.90	BP	3.0	benzene (50%)	85	95	—
	0.90	BP	3.0	—	85	95	—

TABLE III (continued)

Monomer	Monomer [g.]	Initiator		Solvent	Temp. [°C.]	Time [hr.]	Conversion [*ca.* %]
		[Type]	[Wt. % of Monomer]				
Diallylnonanamide	0.89	BP	3.0	benzene (50%)	85	95	—
	0.89	BP	3.0	—	85	95	—
Diallyl-tricyanovinylamine	0.425	BP	3.0	benzene (70%)	85	160	4.0
	0.5	ABN	0.1	benzene (85%)	75	127	3.0

a. BP is benzoyl peroxide
b. TBHP is tert-butylhydroperoxide
c. ABN is α,α'-diazoisobutyronitrile

D. Telomerization Reactions

The workers who have reported addition of polyhalogenated compounds to olefins under free radical conditions would be too numerous to list in this work. However, Kharasch[30] should be mentioned for both his large volume of work as well as his original contribution in this field. An attempt was made in this work to carry out cyclic telomerization reactions on two of the diallylamides by reaction under free radical conditions with chain transfer reagents such as bromotrichloromethane and ethyl bromoacetate. Friedlander[29] has observed in cyclization reactions of this type that the activity of the chain transfer reagent is important in determining the degree to which addition is accompanied by cyclization. Thus, he points out that if an active reagent such as bromotrichloromethane is used, the concentration of the transfer agent must be low to allow cyclization to occur.

A description of the reactions and the results obtained from this study follows.

1. Addition of Ethyl Bromoacetate to Diallylacetamide and Diallylpropionamide

a. Diallylacetamide

Ethyl bromoacetate (0.42 g., 0.00252 mole), diallylacetamide (1.42 g., 0.0102 mole), and benzoyl peroxide (0.14 g.) were dissolved in heptane (14.42 g.) and sealed in a 20 ml. vial. The reaction mixture was heated in an oven at 70° for a period of twenty-four hours.

A dark, oily layer separated out of the reaction mixture which presumably was a mixture of the various adducts possible in the reaction.

b. Diallylpropionamide

Ethyl bromoacetate (21 g., 0.125 mole) and diallylpropionamide (20 g., 0.13 mole) were added dropwise to benzoyl peroxide (1 g.) dissolved in heptane (100 ml.) and contained in a 300 ml., three-necked flask fitted with a stirrer and a reflux condenser. The reaction mixture was heated to reflux with stirring for a twelve hour period. Upon cooling the reaction mixture to room temperature, a dark, viscous oil separated out as a bottom layer.

2. Addition of Bromotrichloromethane to Diallylacetamide and Diallylpropionamide

a. Diallylacetamide

Following the same procedure as in the addition of ethyl bromoacetate the following materials and quantities were used: diallylacetamide (1.42 g., 0.0102 mole), bromotrichloromethane (0.5 g., 0.00268 mole), benzoyl peroxide (0.014 g.), and heptane (14.42 g.). As before, the sealed tube containing the reaction mixture was maintained at 70° for a period of twenty-four hours. A dark, viscous oil resulted.

b. Diallylpropionamide

Diallylpropionamide (200 g., 1.30 mole), bromotrichloromethane (242 g., 1.22 mole), benzoyl peroxide (10 g.), and heptane (1300 ml.) were combined in a 3 liter, three-necked flask fitted with a reflux condenser and a stirrer. The reaction mixture was heated to reflux with stirring for fifteen hours. The reaction mixture was cooled to room temperature and the solvent and unreacted bromotrichloromethane were removed under reduced pressure. The remaining crude reaction product amounted to 324 g. of a viscous, dark oil.

3. Attempted Separation of Adducts

The addition of bromotrichloromethane, or other chain transfer reagents, to the diallylamides can yield any or all of the three possible adducts which contain only one monomer unit. The reaction can yield two one-to-one adducts, one via the cyclic mechanism and one in which only one of the allyl double bonds has undergone reaction. A two-to-one adduct is also possible if both of the allyl double bonds undergo an addition of the chain transfer reagent.

Several attempts were made to separate a cyclic product from the viscous oil obtained by reaction of bromotrichloromethane to diallylpropionamide.

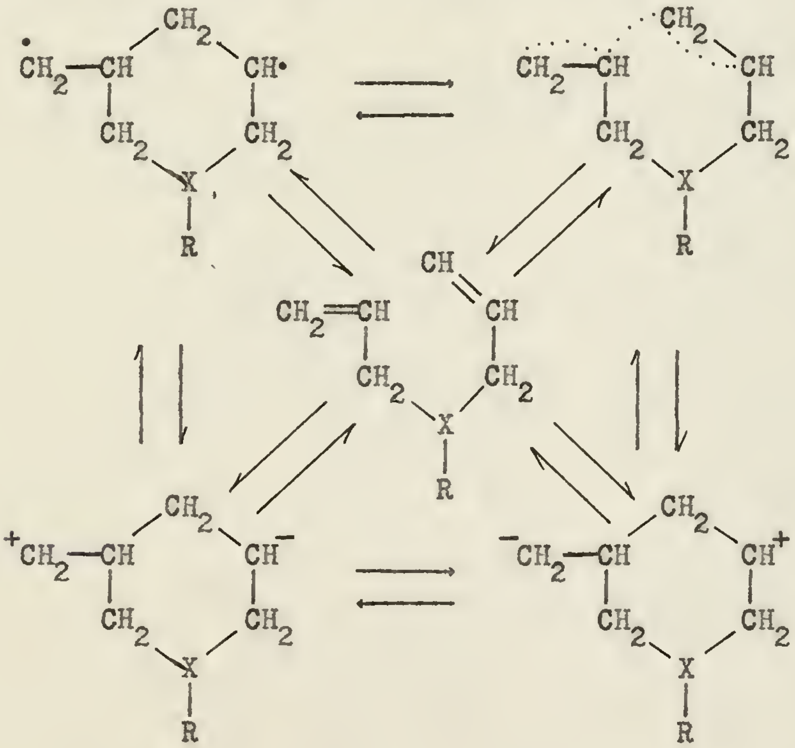
An attempt to separate the mixture by passage through a two inch centrifugal type, molecular still failed to yield definable products. Repeated passage of the reaction product from a typical run through the still gave the following fractions: 1) recovered monomer (33%), 2) viscous, yellow oil (30%), distilled over at less than 200° and 100 microns pressure, and 3) black tar (37%), non-volatile at 200° and 100 microns pressure. Further efforts to obtain good fractions from fraction 2) by successive passage through the still were unsuccessful.

An attempt was also made to separate the reaction mixture by elution chromatography through a column of activated alumina prepared with hexane. A portion of the reaction mixture was dissolved in acetone, filtered to remove any insoluble material, and the acetone evaporated. Ten grams of material so treated was dissolved in 10 ml. of acetone and deposited on the column. The column was eluted in order with the following solvents: hexane, benzene, heptane, butanol, iso-propanol, and acetone. The solvents were gradually changed from one to another. Thus, elution began with hexane, followed with a 25% benzene-75% hexane mixture, etc. The material which was not eluted by hexane, benzene, or heptane but which was eluted by a 15% butanol-85% heptane mixture was collected and amounted to 2.06 g. or 21% of the total. This sample was dissolved in 3 ml. of acetone and deposited on a freshly prepared hexane-alumina column. The column was eluted with heptane, followed with acetone. The acetone-eluted material was separated; and the solvent was evaporated to yield 1.5 g. of a light yellow, viscous oil. The molecular weight of this sample was determined, by measuring the molar depression of the freezing point of benzene, to be 346. The calculated value for a one-to-one adduct is 351.5. An examination of the infrared spectrum of this sample failed to confirm the presence of only the cyclized product. The spectrum differed significantly from the spectrum of the monomer in that the expected absorption for the trichloromethyl group in the 700-800 cm.$^{-1}$ region was present. However the absorption corresponding to the terminal methylene group at 920 cm.$^{-1}$ in the monomer had been split into two separate peaks at 890 and 920 cm.$^{-1}$, and greatly diminished in intensity. Thus, it can only be concluded that the attempt to isolate a pure cyclic adduct was unsuccessful.

CHAPTER IV

INFRARED INVESTIGATIONS OF THE DIALLYLAMIDES AND RELATED COMPOUNDS

One of the stated objectives of this work is to gather evidence to explain the strong tendency of 1,6-heptadienes to undergo polymerization via the cyclic polymerization mechanism. Workers in this laboratory[31] have proposed a structure for the various monomers which involves intramolecular electronic interaction of some sort. This interaction can be represented by the following structure:



The proposed intramolecular interaction is supported by the work of Mikulasova and Hvirik[32] in which they determined that the total activation energy for radical polymerization of diallyldimethylsilane is about 9 kilocalories per mole double bond less than that for allyltrimethylsilane. Additional support for this interaction has been offered by Marvel and Stille.[11] These workers have studied the polymerization of non-conjugated diene systems such as 2,5-dimethyl-1,5-hexadiene by metal alkyl coordination catalysts. This study also included the mono-olefin, 2-methyl-1-pentene, which did not yield high molecular weight materials. The investigators considered both of these systems as 1,1-disubstituted ethylenes and suggested that the driving force afforded by the formation of the cyclic structure was responsible for the success in polymerization of the diene and the lack of success in the case of the mono-olefin.

In the course of this investigation, an examination of the infrared spectra of the several monomers prepared in this study was made. The results of this examination seem to offer additional support for the proposed interaction between the two allyl groups in the monomers.

The infrared spectra were run on a Perkin-Elmer Model 21 double beam spectrometer containing a high dispersion calcium fluoride prism. The spectra were used as confirming evidence for the identification of the diallylamides prepared in the study and contain the absorption frequencies which one would normally expect from this type of compound. The information used as evidence for the proposed interaction was not the appearance or disappearance of any of the expected peaks but rather the pattern exhibited by the observed shifts in frequency of absorption by the amides and related compounds.

The absorption frequencies for the in-plane-deformation vibration of the terminal methylene group in the diallylamide series and related compounds are shown in Table IV.

Bellamy[33] in his comprehensive text on infrared spectra assigns this group to the 1420-1410 cm.$^{-1}$ region and further reports: "...... the band near 1415 cm.$^{-1}$ is usually strong in the infrared and is very stable in position, so that it serves as a useful guide in analysis. The substitution of $-CH_2OR$ and $-CH_2OCOR$ groups has little or no effect upon this frequency, but in case of acrylates and methacrylates it shows a slight fall to 1405 cm.$^{-1}$."

It will be observed from the values in Table IV that there is a definite shift in the frequency of absorption in the series of diallyl compounds listed. This shift may be correlated well with the results from polymerization studies. It is seen that the shift to a higher absorption frequency for the group under consideration parallels the polymerizability of the monomer. Thus, the more readily the monomers undergo polymerization the higher the absorption frequency for the in-plane-deformation vibration of the terminal methylene group.

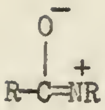
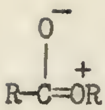
The shifts are not large in absolute magnitude, but the trend which is exhibited seems to be significant. This shift in frequency can probably best be explained by a combination of two electrical effects present in the molecules. These two effects are the inductive effects exerted through the chain, and the mesomeric effect exhibited by the amide group in the sharing of the lone-pair electrons of the nitrogen with the carbonyl carbon atom. Thus, canonical forms such as

TABLE IV

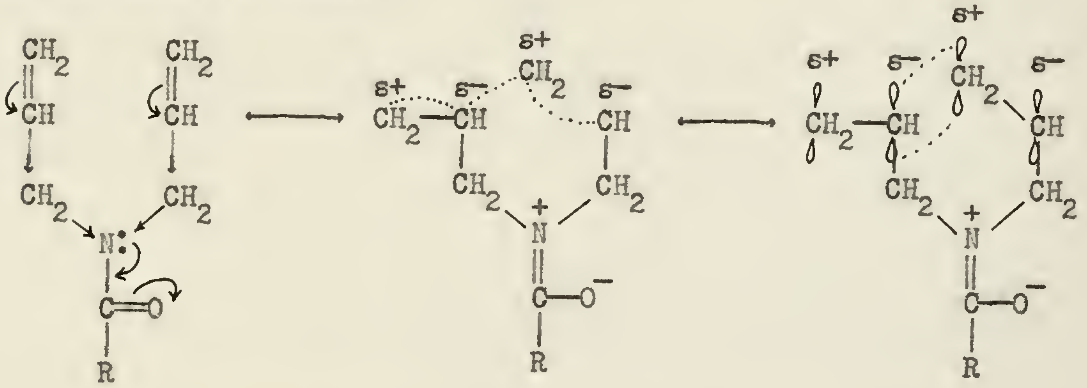
ABSORPTION FREQUENCY OF IN-PLANE-DEFORMATION VIBRATION OF TERMINAL METHYLENE GROUP

Sample	Absorption [μ]	Frequency [cm.$^{-1}$]	Sample Thickness [mm.]
Diallylformamide	7.062	1416	0.015
Diallylacetamide	7.078	1413	0.015
Diallyl-trifluoroacetamide	7.038	1421	0.015
Diallylpropionamide	7.078	1413	0.015
Diallylheptanamide	7.078	1413	0.015
Diallylnonanamide	7.078	1413	0.015
Diallyl-tricyanovinylamine	7.052	1418	0.015
Diallylcyanamide	7.037	1421	0.015
Diallylammonium bromide	6.917[a]	1437[d]	KBr disc
Diallylmethylphosphine oxide	7.040[b]	1420	0.015
Diallylphenylphosphine oxide	7.057[b]	1417	0.015
Diallylmethylphenylphosphonium bromide	7.045[c]	1419	melt
Dimethyl-4-pentene amine	7.080	1411[e]	plates

a. Value from R. Silas, Ph.D. dissertation, University of Florida, June, 1954
b. Sample furnished by Dr. K. D. Berlin
c. Sample furnished by Mr. D. L. Skinner
d. LiF prism
e. NaCl prism


$R-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}R$ and 
$R-\overset{O^-}{\overset{|}{C}}=\overset{+}{O}R$ will contribute to the structure of the amides. Bellamy[34] points out that this contribution is most marked with the amide type of compounds. The combination of these two effects, the mesomeric effect to give a positive charge or at least a partial charge on the nitrogen atom and the inductive effect to distort the electron cloud normally distributed between the terminal carbons, can be offered as plausible support for structures of possible forms supporting the proposed interaction between the two allyl groups.

Thus, the combination of the two electrical effects may be illustrated as follows:



The definite trend in the amide series, that of increasing polymerizability with decreasing basicity of the nitrogen atom, is further born out by inclusion of the quaternary ammonium salt which is the least basic of the series, and the most polymerizable. Absorption occurs at the highest frequency in this compound.

Several other compounds are included in the table on which polymerization reactions have not been run but which seem to fit in well with the trend of absorption frequency and the usually accepted electron withdrawing power of the groups substituted on the central nitrogen atom.

CHAPTER V

STUDIES ON POLY-(METHACRYLIC ANHYDRIDE)

Workers in both these[4] and other laboratories[14,15] independently demonstrated that acrylic anhydride could be polymerized via the cyclic polymerization mechanism to yield linear, soluble polymers. This was the first evidence that monomers, usually considered as highly reactive monomers, could be polymerized in such a manner. Jones[16] has also described poly-(diacrylylmethane) resulting from an attempted Claisen condensation of methyl vinyl ketone with ethyl acrylate in an attempt to prepare the monomer diacrylylmethane. He attributed the result to an anionic polymerization of the monomeric compound as it was formed.

Stereoregular polymers have been prepared under a variety of conditions to yield polymers of vastly different properties than so called "atactic" or random polymers. An excellent review of this field is available in the text by Gaylord and Mark, Linear and Stereoregular Addition Polymers.[35] Until recently the bulk of the stereoregular polymers prepared had resulted from anionic, cationic or Ziegler-type coordination catalysts. The work by Crawshaw[4] demonstrated that there may be some stereoregulating influence in the cyclic polymerization mechanism. He obtained poly-(acrylic acid) by hydrolysis of poly-(acrylic anhydride) which was substantially more crystalline than conventional poly-(acrylic acid) as demonstrated by x-ray diffraction studies.

In this work, methacrylic anhydride was polymerized via the cyclic polymerization mechanism to poly-(methacrylic anhydride) under a variety of conditions. This was undertaken in an effort to determine whether any stereo-control is exerted via this mechanism and if so to what extent this stereo-control will manifest itself in the configuration of the polymers so prepared.

Some time after this work was undertaken, Bovey and Tiers[36] observed that the nuclear magnetic resonance (NMR) spectra of poly-(methyl methacrylate) in chloroform solution at 90° showed three α-methyl proton peaks. They determined that these three peaks correspond to those α-methyl groups in isotactic, heterotactic and syndiotactic placements. The terms above, denoting the stereo configuration of the polymer segments, have been redefined by Bovey in his paper. Thus, he terms an isotactic configuration as one which the α-methyl group is flanked on both sides by units of the same configuration. This gives rise to the peak at lowest field strength. A heterotactic configuration is designated as one in which the central α-methyl group is flanked on one side by a similar configuration and on the other by a dissimilar configuration, and results in the middle peak observed. The syndiotactic configuration is defined as one in which the central α-methyl group is flanked on each side by monomer units of the opposite configurations, and is observed as the peak at highest field strength. Thus, in this system isotactic configurations are described as lll or ddd units, heterotactic configurations as ldd, dll, ddl, or lld units and syndiotactic configurations as ldl or dld units. The area described by each peak will be proportional to the number of isotactic, heterotactic and sydiotactic units.

This method of analysis lends itself well to this problem since Fox and his co-workers[37,38] have prepared samples of isotactic and syndiotactic poly-(methyl methacrylate) of nearly pure stereoregular configurations. These workers also determined the identity of each type by independent x-ray analysis. This work made it possible for Bovey to assign the various peaks observed in the NMR spectra to the α-methyl protons in the three types of configurations.

In this section a description is given of the polymerization of methacrylic anhydride under various conditions and the results obtained from NMR investigation of poly-(methyl methacrylate) derived from the poly-(anhydride) by hydrolysis to the poly-(acid) and subsequent esterification.

A. Materials

The solvents used in this study were all dried prior to use. Benzene (reagent grade), ethyl ether and hexane were from stock and were dried over sodium ribbon. Methanol was also from stock and was distilled from sodium metal before use. Dimethylformamide, purchased from Matheson, Coleman and Bell, was distilled and stored over Drierite. Methacrylic anhydride, purchased from The Borden Company, was distilled before use; and gas chromatographic and infrared analysis indicated that its composition of a single component was in excess of 97%. The remaining materials were also purchased: benzoyl peroxide from the Lucidol Division, Wallace and Tiernan, Incorporated; α,α'-diazoisobutyronitrile from Eastman Organic Chemicals; N-methyl-nitrosourea from K and K Laboratories; and chloroform, spectroanalyzed grade, from Fisher Scientific Company.

B. Polymerization Procedure

Measured volumes of the monomer and solvent along with weighed quantities of initiator, α,α'-diazoisobutyronitrile, were sealed in 20 ml. ampoules after cooling in a Dry-Ice-acetone mixture and flushing with dry nitrogen gas. Polymerizations were carried out in a water bath maintained at a temperature constant within ± 0.1° for the period of time indicated. In those runs in which the samples were irradiated with ultraviolet light the source was a Blak-Ray Model x-4 lamp placed approximately 8 cm. away from the sample vial. This procedure was followed in all of the polymerizations except those in which the solvent was dimethylformamide. In these experiments the samples were contained in a 25 ml. tube fitted with a gas inlet tube arranged to bubble nitrogen gas through the solution during the course of the reaction. The samples were irradiated and maintained at the indicated temperatures in the same manner as previously described. The polymers were freed from monomer and solvent by trituration with methanol. The polymers were then filtered and dried *in vacuo*. A number of the polymers were dissolved in dimethylformamide and precipitated by addition to ethyl ether or methanol in order to demonstrate that the poly-(methacrylic anhydride) so prepared was a soluble polymer. The polymers dissolved very slowly in dimethylformamide with solution usually requiring from forty-eight to seventy-two hours in a closed system.

The results of the polymerizations are summarized in Table V.

C. Hydrolysis to Poly-(Methacrylic Acid)

The samples prepared above were hydrolyzed to yield poly-(methacrylic acid). The general procedure used in the hydrolysis reaction is outlined below. There is also included in this section a description of the conditions used in comparative hydrolysis studies which were undertaken in an effort to demonstrate that the conditions employed during hydrolysis did not affect the configuration of the pseudo-asymmetric carbon atoms in the final product, poly-(methyl methacrylate). This would be true if no racemization occurs during the course of the hydrolysis reaction. The NMR measurements which are given in a later section demonstrated that this was indeed the case and similar poly-(anhydride) samples gave NMR measurements very nearly the same in each case regardless of the method of hydrolysis employed. The results of the hydrolysis of poly-(methacrylic anhydride) to yield poly-(methacrylic acid) are summarized in Table VI.

1. General Procedure

Poly-(methacrylic anhydride) was added to distilled water in a flask fitted with a reflux condenser. The water to polymer ratio (volume/weight) was approximately 100 ml./1 g. in each case. The mixtures were allowed to stand at room temperature overnight and then

TABLE V

RESULTS OF METHACRYLIC ANHYDRIDE POLYMERIZATIONS

Sample Number	Temperature [°C.]	Initiator [wt. %]	Time [hr.]	% Conversion
33-D[a]	1	1.0	19	78
33-C[a]	20	1.0	14.5	96
33-B[a]	30	1.0	7.3	68
31-D	30	1.0	22	33
33-A	40	1.0	3	45
31-A	50	1.0	2	37
31-B	60	1.0	1.5	70
31-E	70	1.0	0.5	75
31-F	80	1.0	0.22	88
6	65	1.0[b]	—	—
21	15	0.25[c]	2	46

a. Irradiated with ultraviolet lamp.
b. Benzoyl peroxide initiator, 25% solution of monomer in benzene. Sample prepared by M. D. Barnett.
c. Benzoin as photoinitiator

TABLE VI

HYDROLYSIS OF POLY-(METHACRYLIC ANHYDRIDE) TO POLY-(METHACRYLIC ACID)

Sample Number	Weight [g. polymer]	Volume [ml. water]	Yield [g. poly-(acid)]	% Recovery
31-A	0.30	100	0.23	69
31-B	0.25	25	0.20	72
31-C	0.20	100	0.17	75
31-D	0.30	100	0.31	92
31-E	0.25	25	0.22	79
31-F	0.25	25	0.19	76
33-A	0.40	100	0.34	76
33-B	0.50	100	0.37	66
33-C	0.25	25	0.20	72
33-D	0.50	100	0.39	70
34-A[a]	1.00[b]	50	—	—
34-B[a]	1.00[c]	50	—	—
34-C[a]	1.00[d]	50	—	—

a. Identical samples hydrolyzed under different conditions.
b. Mild hydrolysis, see text.
c. Hydrolyzed by General Hydrolysis Procedure, see text.
d. Basic hydrolysis, see text.

refluxed for approximately twenty-four hours. After refluxing, the solutions were allowed to stand for an additional twenty-four hours. The solutions were then filtered through a medium-porosity, sintered glass filter and the water evaporated under heat of an infrared lamp and reduced pressure employing a Lab-Drier. The resulting clear films of poly-(methacrylic acid) were removed from the flasks, ground to a fine powder, and dried *in vacuo* for a period of at least twenty-four hours.

2. Basic Hydrolysis

Poly-(methacrylic anhydride) (1 g.) was added to 50 ml. of distilled water and the mixture made strongly basic by addition of (solid) sodium hydroxide pellets. The mixture was stirred for a few minutes until solution was complete. The solution was filtered and the clear filtrate heated almost to boiling. To the hot solution, concentrated hydrochloric acid was added dropwise until the solution became strongly acid. The coagulated solid portion was stirred and removed from the acidic solution. The solid mixture of poly-(methacrylic acid) and sodium chloride was dried *in vacuo* overnight, ground to a fine powder and then redried *in vacuo* for twenty-four hours.

3. Mild Hydrolysis

Poly-(methacrylic anhydride) (1 g.) was added to 50 ml. of distilled water and stirred at room temperature until solution was completed. The solution was filtered and the water removed *in vacuo*. The resulting poly-(methacrylic acid) was ground to a fine powder and dried *in vacuo* for a period of twenty-four hours.

D. Esterification of Poly-(Methacrylic Acid)

The poly-(methacrylic acid) samples were converted to poly-(methyl methacrylate) following the method of Katchalsky.[39] The diazomethane was prepared in a benzene solution by basic decomposition of methylnitrosourea according to the method given in Organic Syntheses.[40] An outline of the general method used is given below and the results of the various preparations are summarized in Table VII.

A sample of poly-(methacrylic acid) (0.205 g., 0.0012 mole) contained in a 50 ml. test tube was covered with a benzene solution of diazomethane (20 ml., 5.6 g./300 ml.). The tube was stoppered with a loose fitting cork and allowed to stand overnight at room temperature. At the end of a fifteen hour period the solution was essentially colorless but some gelatinous material, presumably unreacted poly-(methacrylic acid), was evident in the bottom of the benzene solution. A second addition of diazomethane solution (20 ml., 5.6 g./200 ml.) was made after the initial fifteen hour reaction period. After the second addition of diazomethane solution, the reaction mixtures were stirred at thirty minute intervals for three hours and then allowed to stand overnight at room temperature. The reaction mixtures were filtered through a high speed filter paper on a Buchner funnel. The unreacted material was washed on the filter with 50 ml. of benzene and the washings combined with the original filtrate.

The poly-(methyl methacrylate) was isolated by dropwise addition of the benzene solution (ca. 80 ml.) to four times its volume of rapidly stirred hexane. The hexane-polymer mixtures were centrifuged

TABLE VII

CONVERSION OF POLY-(METHACRYLIC ACID) TO POLY-(METHYL METHACRYLATE) BY REACTION WITH DIAZOMETHANE

Sample Number	[mole diazomethane/ mole poly-(acid)]	Volume [ml. benzene]	Yield [g. poly-(ester)]	% Conversion
31-A	19	40	0.17	71
31-B	23	40	0.10	50
31-C	37	50	0.05	31
31-D	23	40	0.15	75
31-E	21	40	0.11	53
31-F	23	40	0.14	74
33-A	12.5	50	0.33	83
33-B	12	50	0.34	81
33-C	16	30	0.09	45
33-D	11	50	0.36	82
34-A	6.5	50	0.54	73
34-B	5	35	0.44	60
34-C	7.5	45	0.45	56

and the hexane decanted. The poly-(methyl methacrylate) was dried in vacuo for at least twenty-four hours.

E. X-Ray Diffraction Studies

Sufficient poly-(methyl methacrylate), prepared as described in the previous sections, was dissolved in benzene to prepare a solution of approximately 2% concentration. This solution was allowed to evaporate slowly at room temperature from a shallow cup formed from aluminum foil to yield a slightly opaque film. The poly-(methyl methacrylate) had been prepared at 65° with benzoyl peroxide as the initiator. This sample had a molecular weight of 124,000 as determined by viscosity measurements, using the relationship of Baxendale, Bywater and Evans.[41]

The film was dried in vacuo at room temperature for several days and then at higher temperatures, up to 90°, for several hours at approximately thirty degree intervals. This film was submitted to Dr. W. F. Loranger at the General Electric X-Ray Laboratories for x-ray diffraction measurements. A Laue diffraction pattern showed four distinct diffraction lines. A diffractometer trace showed broad, diffuse peaks at 14° to 16° and 28° to 30° and also sharp peaks at 21.5° and 24.1°. The patterns, as interpreted by Dr. Loranger, indicate that the sample was approximately 50% crystalline.

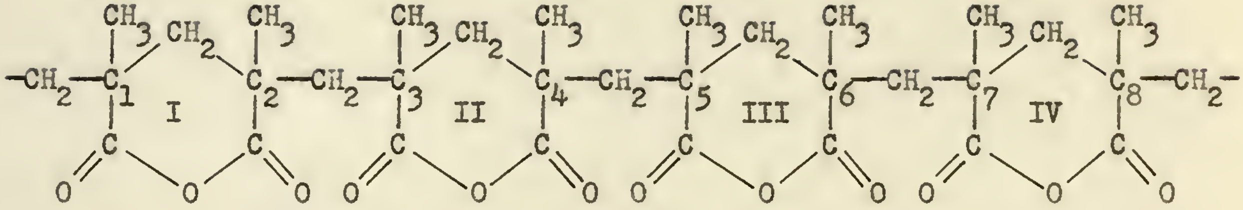
F. Nuclear Magnetic Resonance Studies

Included in this section are the general methods of sample preparation, measurements and a discussion of the results as well as a discussion of the relationships between the various stereo configurations possible in the polymers.

An examination of molecular models of the poly-(methacrylic anhydride) polymers prepared from the LaPine-type models shows that all three of the possible types of configurations can be constructed. Of the models of the three configurations, isotactic, syndiotactic and heterotactic, that of the isotactic polymer was the easiest to construct and seemed to be the least sterically hindered. In all of the models there seemed to be considerable steric hinderance between α-methyl groups on adjacent anhydride rings. The models also indicated that in the isotactic polymer the carbonyl oxygen atoms are quite close while the preferred arrangement in the syndiotactic and heterotactic polymers was one in which the carbonyl oxygen atoms on adjacent rings are farther apart from one another. This would place the anhydride portion of one ring in the same relative position as the cyclic methylene group in the next ring.

An examination of models of the various polymer segments with respect to the methylene group connecting adjacent cyclic anhydride units indicated that it was possible for the methylene groups to assume all of the several possible conformational arrangements. Thus, the methylene group could be in an axial-axial, equatorial-equatorial, axial-equatorial or equatorial-axial conformation with respect to the two rings which it joined together. This relationship is an extension of the above discussion inasmuch as the fixing of the conformation of the methylene group between two rings fixes the configuration of the pseudo-asymmetric carbon atoms. An examination of the above would show that an axial-axial or equatorial-equatorial conformation would lead to an isotactic configuration for the polymer. An axial-equatorial conformation would lead to alternation of configuration and gives rise to heterotactic or syndiotactic polymer segments. A third placement is necessary in each case to define an isotactic, syndiotactic or heterotactic unit.

Thus, a polymer which is predominantly isotactic will be biased toward successive placements or conformations being the same as the preceding one. A conformation in which the methylene group is axial to one ring and equatorial to the other or a conformation in which one methylene group attached to a ring is axial and the other methylene group attached to the same ring is equatorial would lead to alternation of configuration of the pseudo-asymmetric carbon atom. If these sequences are favored over those which are opposite to them then the probability of a syndiotactic placement will exceed the probability of a heterotactic placement. The probability of a heterotactic placement would be the larger if a syndioduotactic structure as proposed by Hwa[42] predominated. In this case there would be a bias toward an axial-axial-equatorial-equatorial sequence. This sequence can arise from either of two types of conformations as in the case of the syndiotactic sequences.



The methylene group connecting rings I and II would be equatorial at positions 2 and 3 while the methylene group connecting rings II and III would be axial at positions 4 and 5. The other sequence would be one in which the methylene group connecting rings I and II is axial at position 2 and equatorial at position 3 while the methylene group connecting rings II and III is equatorial at position 4 and axial at position 5.

Coleman[43] and Bovey[36] have derived the relationships of the various probabilities in random chain growth. They designate by α the probability that a growing chain will add a monomer unit to give the same configuration as that of the unit at the growing end. The assumptions are made that α is controlled by only the configuration of the end unit and not by the preceding one and that the propagation is adequately described by a single value of α. The probabilities (P) are: $P_i = \alpha^2$, $P_s = (1 - \alpha)^2$ and $P_h = 2(\alpha - \alpha^2)$. The subscripts i, s and h refer to isotactic, syndiotactic and heterotactic placements, respectively. Figure 1 is a plot of these relationships. Bovey[36] has compared the results of free radical polymerizations of methyl methacrylate to anionic polymerizations of methyl methacrylate as described by Fox.[37] He determined that "atactic" poly-(methyl methacrylate) or material polymerized by free radical initiators is predominantly syndiotactic (77-87%) in character. These polymers fit the probability curves well

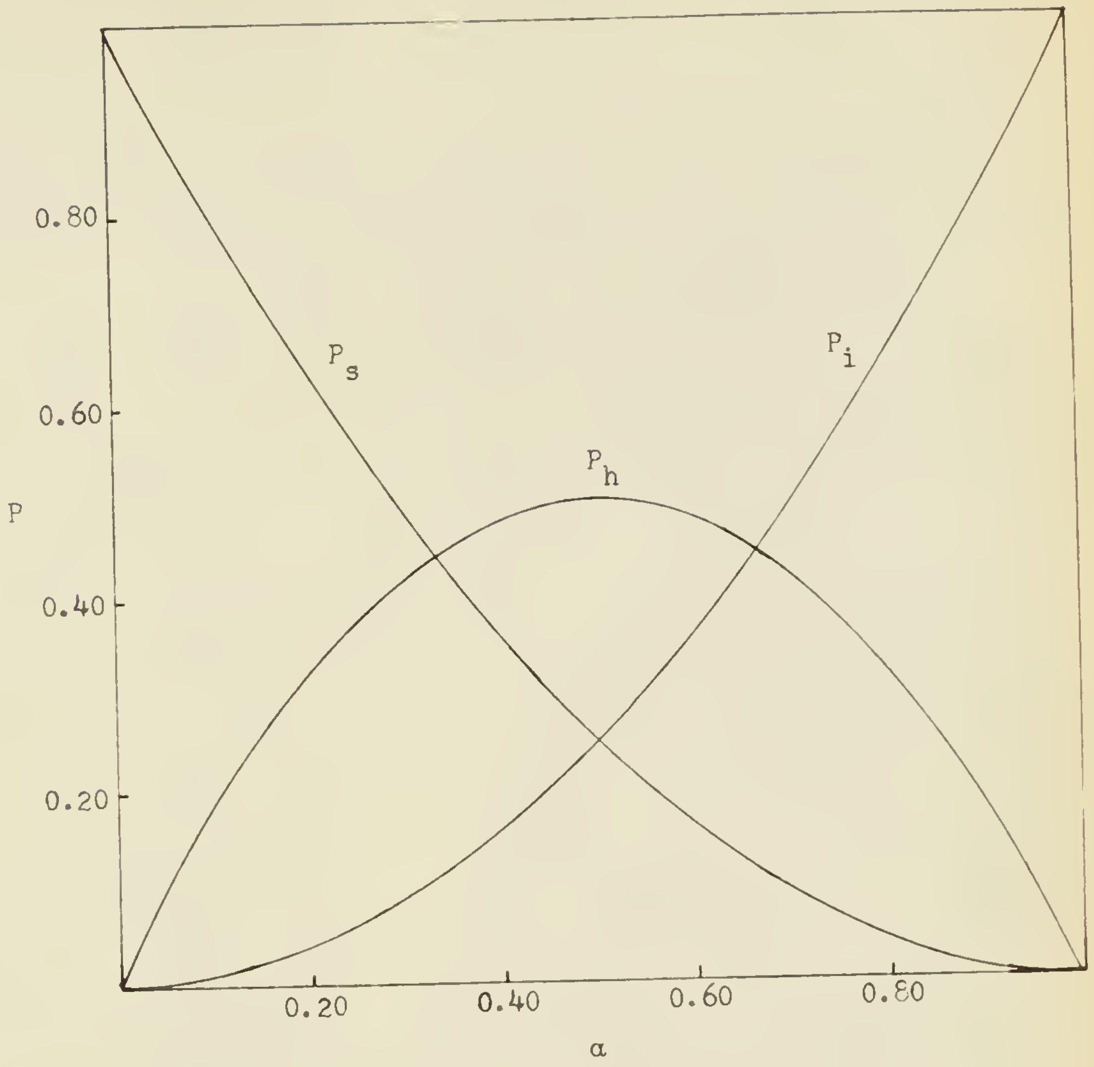


Figure 1. The probabilities of occurrence of isotactic, P_i, heterotactic, P_h, and syndiotactic, P_s, sequences of monomer units as a function of α, the probability of isotactic placement of monomer units during propagation.

and thus the assumptions seem to be valid in this case. However, the poly-(methyl methacrylate) samples prepared using anionic initiators did not fit the probability curves and these were termed "non-sigma" systems or systems not described by a single probability value. He attributed the failure to the tendency of the metal ion to complex with both the solvent system and the growing chain.

Workers in this field have also observed that solvents and temperature both affect the stereo-control in polymerization systems in type and degree. It has been shown in all previous work that a decrease in temperature is accompanied by an increase in stereoregularity in the products in both anionic[36] and free radical polymerizations.[36,44,45] It has also been observed, in both anionic[37] and free radical[44] polymerizations that the solvent determines to a large extent which form of polymer results. In the polymerization of methyl methacrylate with toluene as the solvent anionic initiators yield isotactic products; with polar solvents such as dimethoxyethane the syndiotactic products are formed; while in systems of mixed solvents such as toluene-dimethoxyethane a large proportion of all three configurations results.

As a result of the above observations the main portion of this work constitutes a study of the effect of temperature of polymerization on the stereoregularity of the products obtained.

1. Preparation of NMR Samples

The poly-(methyl methacrylate) described in the previous sections, along with several samples for comparative purposes, were used in this work. Weighed quantities of the polymers were placed in 5 mm. (O.D.) Pyrex glass tubes approximately 9 in. long and sealed at one end.

Sufficient spectroanalyzed chloroform was added to give a 20% (w/v) mixture. The tubes were sealed and the mixture heated in a water bath at 100° to facilitate solution of the polymers. A few of the samples failed to give a homogeneous solution and were subsequently diluted by addition of solvent in order to get useful results from the NMR measurements. The concentrations are listed in Table VIII with the NMR results.

2. Measurements

The NMR spectra were run on a Varian V-4302 high resolution spectrometer, operating at 56.4 megacycles. The temperature of the samples was maintained at 90-98° during the measurements.

The relative peak areas were determined by visual division of the overlap area and measuring the designated areas with a planimeter. The results obtained in this manner suggested that the area described by each peak was proportional to the three-halves power of the peak heights. Since the second method was deemed the most reproducible as well as the most rapid, it was used in all of the measurements recorded. Several traces of the α-methyl proton peaks were obtained in each case and the average values of the peaks are recorded. The results of the measurements are shown in Table VIII.

G. Interpretation of Results

Figure 2 is a plot of the percentage of isotactic units in the poly-(methyl methacrylate) samples versus the polymerization temperature.

TABLE VIII

FRACTIONS OF POLY-(METHYL METHACRYLATE) IN THE THREE STEREO CONFIGURATIONS AS DETERMINED BY NMR

Sample Number	Polymerization Temperature [°C.]	Concentration [g./ml.]	i [%]	h [%]	s [%]	α [based on i peak]
33-D	1	0.20	17.9	43.5	38.6	0.420
33-C	20	0.10	31.3	38.5	30.2	0.557
33-B[a]	30	0.15	24.2	40.7	33.9	0.560[a]
31-D[a]	30	0.10	39.0	31.5	29.2	0.560[a]
33-A	40	0.14	34.0	35.7	30.2	0.583
31-A	50	0.20	35.8	36.3	28.0	0.597
31-B	60	0.20	42.4	32.2	25.5	0.655
31-E	70	0.10	49.3	29.2	21.5	0.705
31-F	80	0.10	66.7	20.3	13.0	0.815
34-A	65	0.20	18.9	48.3	32.8	0.435
34-B	65	0.20	20.8	47.8	31.3	0.455
21	15	0.22	7	44	48	0.265
9-1	- 80[b]	0.26	78	11	11	0.882
40 [c]	100	0.15	3.2	14.5	82.3	0.090
41 [d]	- 70	0.15	0	5.0	95.0	0.02

a. Average of the two 30° samples plotted.
b. Sample prepared by Dr. H. G. Clark, n-butyl lithium in toluene.
c. Value from F. A. Bovey, benzoyl peroxide initiator in toluene.
d. Value from F. A. Bovey, sodium naphthalene in glyme solution.
b,c,d. This refers to polymerization of methyl methacrylate.

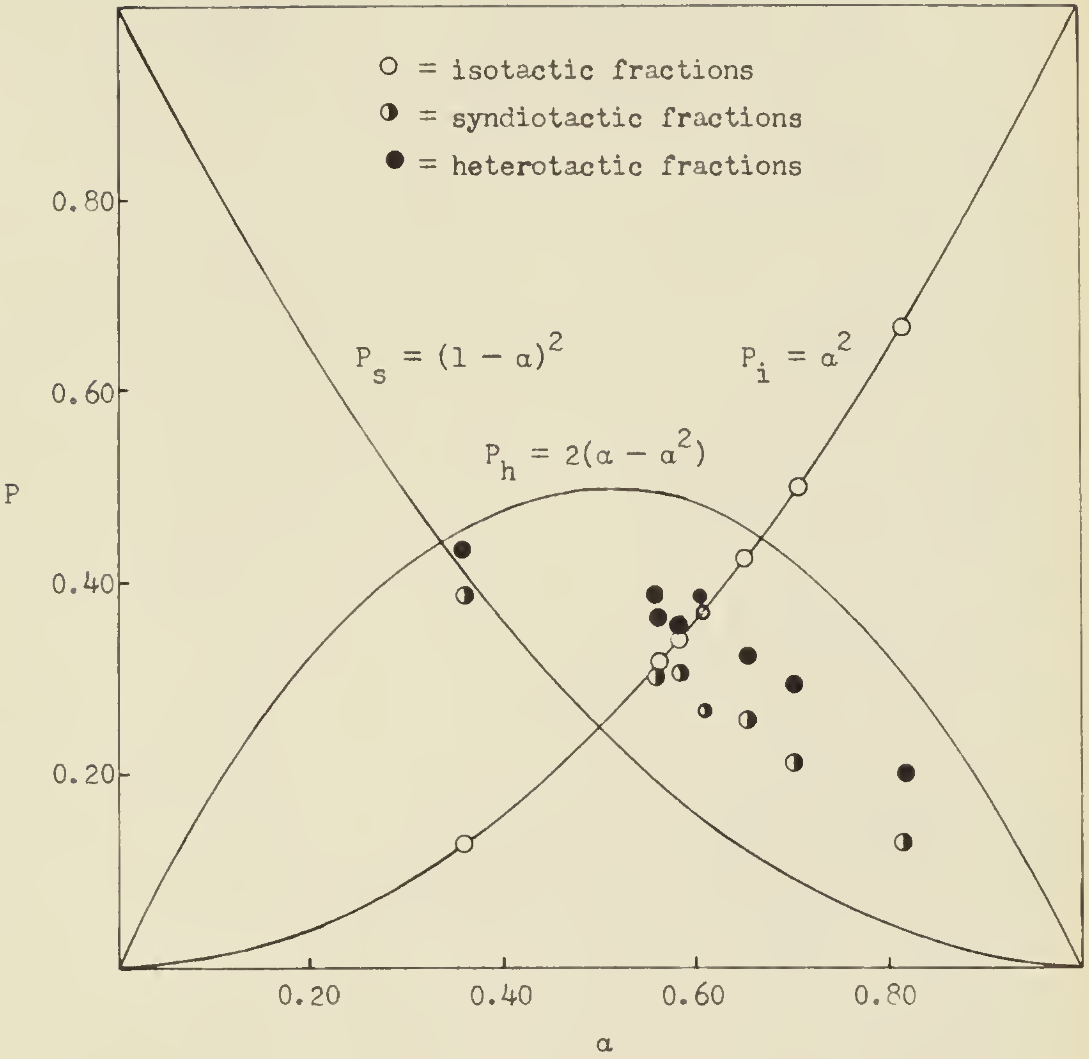


Figure 2. The probabilities of occurrence of isotactic, heterotactic and syndiotactic sequences of monomer units as a function of α, the probability of isotactic placement of monomer units during propagation. The fraction of isotactic is placed on the isotactic line to determine the value of α.

This group of samples is listed in Table VIII. All of these samples were prepared under identical conditions except for the temperature of polymerization and the fact that some of the samples prepared at low temperatures were irradiated with ultraviolet light. The trend is unmistakable. There is a definite increase in the percentage of isotactic character with an increase in temperature.

In Figure 3, a plot of the probability values, the results of the same series of polymerizations are plotted on the curves. The observed value for the isotactic point is placed on the isotactic plot and the values for per cent syndiotactic and heterotactic placements are allowed to fall where they may. It is quite obvious that the syndiotactic and heterotactic points do not fall within acceptable limits of their predicted values. From this it can only be concluded that this system is a "non-sigma" system as described by Bovey. However, the cause for the failure in this case must be ascribed to the failure of the assumption that the placement is unaffected by the penultimate unit. It can be concluded from this that the cyclic mechanism does indeed affect the steric path in polymerization reactions and it may even do so in a different manner that is observed in conventional mechanisms.

It has previously been pointed out, in a prediction by Huggins[46] in 1944, that a preponderance of segments of chains of either isotactic or syndiotactic configuration may arise in homogeneous free radical polymerizations if the free energy of activation for an isotactic placement[43] is different from that for a syndiotactic placement.

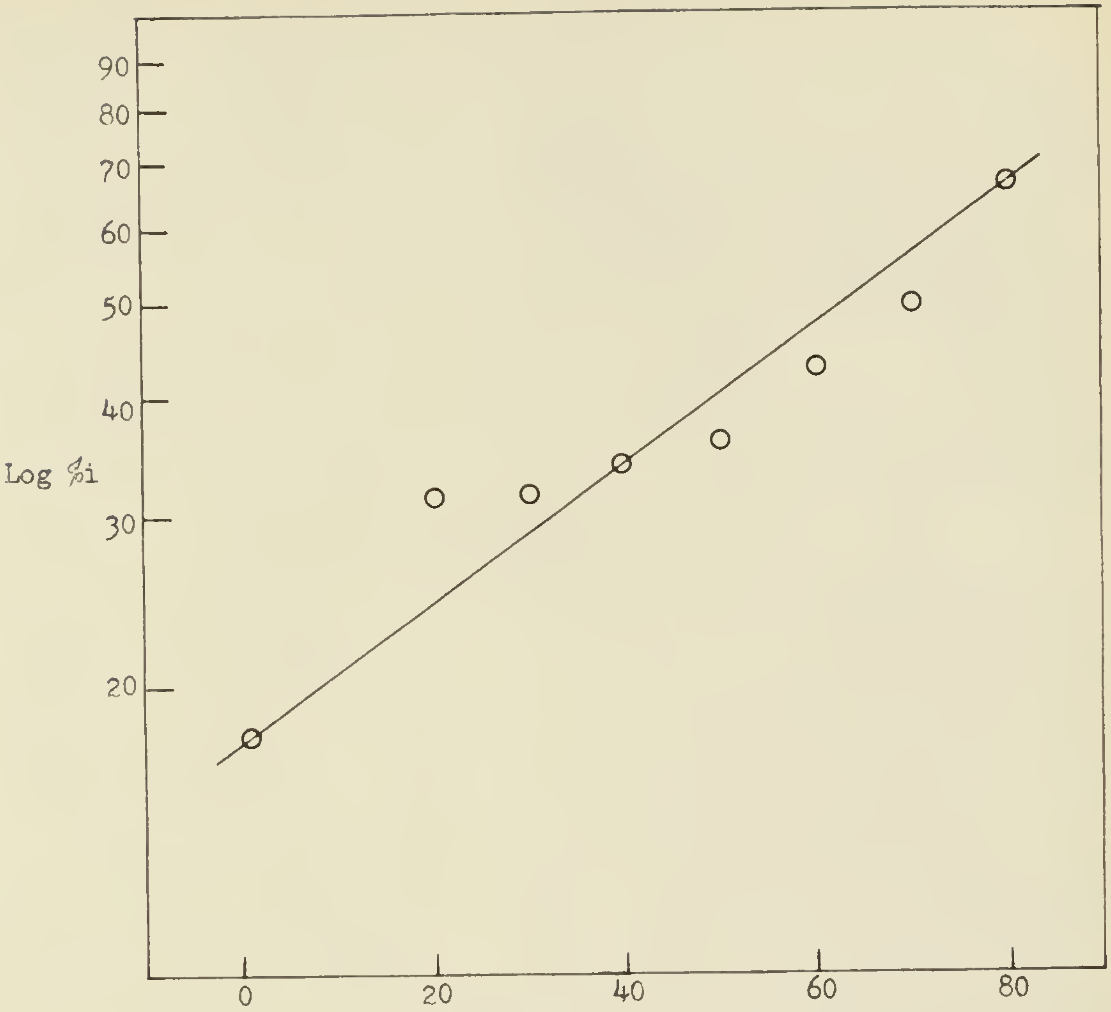


Figure 3. Plot of log of the percentage of isotactic fraction in the poly-(methyl methacrylate) samples versus the temperature of polymerization.

This has been developed to some extent by Fox and co-workers[45] in their work on free radical polymerization of methyl methacrylate.

In the analysis by Fox[45] the suggestion was made that an isotactic placement, in the polymerization of methyl methacrylate, may be more favored with relation to energy while the syndiotactic placements are more favored with relation to entropy. If the reactions are kinetically controlled the parallel reasoning may be applied in this work. However, since the opposite results are observed in the polymerization of methacrylic anhydride via the cyclic mechanism, the isotactic placement would be less favored with respect to energy and more favored with respect to entropy. The numerical interrelation of these two factors, which are influenced by the steric considerations mentioned earlier, determines the free energy of activation for the polymerization process and thus the temperature dependency of the stereoconfiguration of the polymeric products.

An alternative explanation, if the reactions are controlled by both kinetic and equilibrium considerations, may also be offered. If a combination of these two factors do control the polymerization, then an examination of the results would lead to the following conclusion. In view of the fact that the isotactic structure predominates at the higher temperatures while the more random results are observed at lower temperatures, the syndiotactic structure seems to be the more readily formed, in a kinetic sense, while the isotactic structure is the thermodynamically more stable configuration.

CHAPTER VI

SUMMARY

Three areas of interest concerning the polymerization of diene monomers via a cyclic polymerization mechanism were investigated. These considerations are: 1) the relation of the structure of the monomer to the polymerizability of the monomer, 2) the determination of the existence of stereo regulation via this mechanism and, 3) the investigation of the extent of this stereo regulation in a polymerization system.

A series of diallylamides, some of which had not been previously reported, were prepared and the physical constants of these compounds are listed. A structurally related compound, N,N-diallyl-N-tricyanovinylamine was also prepared. Included in this study was an investigation of the infrared spectra and the polymerizability of the diallyl substituted compounds. A correlation of the results of the polymerization study and infrared investigation is offered. This correlation is presented as substantiating evidence for an intramolecular interaction in the monomeric compounds which is believed to offer a partial explanation for the success of the accepted intramolecular-intermolecular cyclic polymerization mechanism.

Methacrylic anhydride was polymerized, in high yields, at temperatures ranging from 1° to 80°, in benzene solution, to linear, soluble polymers. The poly-(methacrylic anhydride) so prepared was hydrolyzed to the corresponding poly-(methacrylic acid) and this poly-(acid) esterified by reaction with diazomethane to yield poly-(methyl methacrylate). The result of an x-ray diffraction study of an unstretched film of poly-(methyl methacrylate) prepared in a similar manner is given. The determination of the fraction of the polymer present in each of the three possible stereo configurations, isotactic, syndiotactic and heterotactic, was made from a nuclear magnetic resonance investigation of the derived poly-(methyl methacrylate). The results indicate that the stereo configuration is influenced by the cyclic polymerization mechanism. The results also indicate that there is a bias toward increasing isotactic character in the polymers with an increase in polymerization temperature. Two possible explanations are offered. One in terms of a kinetic control of the steric placements and the other in terms of a balance between equilibrium and kinetic considerations.

BIBLIOGRAPHY

1. Butler, G. B., and Ingley, F. L., *J. Am. Chem. Soc.*, *73*, 894 (1951).
2. Butler, G. B., and Angelo, R. J., *J. Am. Chem. Soc.*, *79*, 3128 (1957).
3. Butler, G. B., Crawshaw, A., and Miller, W. L., *J. Am. Chem. Soc.*, *80*, 3615 (1958).
4. Crawshaw, A., and Butler, G. B., *J. Am. Chem. Soc.*, *80*, 5464 (1958).
5. Barnett, M. D., Crawshaw, A., and Butler, G. B., *J. Am. Chem. Soc.*, *81*, 5946 (1959).
6. Berlin, K. D., and Butler, G. B., *J. Am. Chem. Soc.*, *82*, 2712 (1960).
7. Butler, G. B., Skinner, D. L., and Stackman, R. W., Conference on High Temperature Polymer and Fluid Research, WADC, Dayton, Ohio, May, 1959.
8. Oiwa, M., and Ogata, J., *J. Am. Chem. Soc. Japan*, *79*, 1506 (1958).
9. Marvel, C. S., and Vest, R. D., *J. Am. Chem. Soc.*, *79*, 5771 (1957).
10. Marvel, C. S., and Vest, R. D., *J. Am. Chem. Soc.*, *81*, 984 (1959).
11. Marvel, C. S., and Stille, J. K., *J. Am. Chem. Soc.*, *80*, 1740 (1958).
12. Marvel, C. S., Kiener, P. E., and Vessel, E. D., *J. Am. Chem. Soc.*, *81*, 4694 (1959).
13. Marvel, C. S., and Garrison, W. E., Jr., *J. Am. Chem. Soc.*, *81*, 4737 (1959).
14. Jones, J. F., *J. Polymer Sci.*, *33*, 15 (1958).
15. Jones, J. F. (to B. F. Goodrich Company), *Italian Patent 563,941*, June 7, 1957.
16. Jones, J. F., *J. Polymer Sci.*, *33*, 7 (1958).

17. Jones, J. F., *J. Polymer Sci.*, *33*, 513 (1958).

18. Field, N. D., *J. Am. Chem. Soc.*, *82*, 0000 (1960).

19. Furst, A., Cutting, W. C., and Gross, H., *Cancer Research*, *15*, 294 (1955); *Chem. Abstracts*, *49*, 16225 (1955).

20. Adams, F. H., (to American Cyanamid Company), *U.S. Patent 2,479,890*, August 23, 1949; *Chem. Abstracts*, *43*, 9473 (1949).

21. Hickinbottom, W. J., *Reactions of Organic Compounds*, 2d ed., Longmans, Green and Co., London (1948).

22. Shirley, D. A., *Preparation of Organic Intermediates*, p. 258, John Wiley and Sons, Inc., New York (1951).

23. McKusick, B. C., Heckert, R. E., Cairns, T. L., and Coffman, D. D., *J. Am. Chem. Soc.*, *80*, 2806 (1958).

24. Simpson, W. Holt, T., and Zeite, R., *J. Polymer Sci.*, *10*, 489 (1953).

25. Simpson, W., and Holt, T., *J. Polymer Sci.*, *18*, 335 (1955).

26. Haward, R. N., and Simpson, W., *J. Polymer Sci.*, *18*, 440 (1955).

27. Price, J. A. (to American Cyanamid Company), *U.S. Patent 3,871,229*, January 27, 1959.

28. Schuller, W. H., Price, J. A., Moore, S. T., and Thomas, W. M., *J. Chem. Eng. Data*, *4*, 273 (1959).

29. Friedlander, W. S., Paper No. 29, p. 18N, Division of Organic Chemistry, ACS Meeting, San Francisco, April, 1958.

30. Kharasch, M. S., Jensen, E. W., and Urry, W. H., *Science*, *102*, 128 (1945).

31. Butler, G. B., Brooks, T. W., and Miller, W. L., Paper Presented at the International Symposium on Macromolecular Chemistry, Moscow, U.S.S.R., June, 1960.

32. Mikulasova, O., and Hvirik, A., Chemische Zvesti, 11, 641 (1957).

33. Bellamy, L. J., The Infra-red Spectra of Complex Molecules, 2d ed., p. 53, John Wiley and Sons, Inc., New York (1959).

34. Bellamy, L. J., The Infra-red Spectra of Complex Molecules, 2d ed., p. 395, John Wiley and Sons, Inc., New York (1959).

35. Gaylord, N. G., and Mark, H. F., Linear and Stereoregular Addition Polymers, Interscience Publishers, Inc., New York (1959).

36. Bovey, F. A., and Tiers, G. W. D., J. Polymer Sci., 44, 173 (1960).

37. Fox, T. G., Garrett, B. S., Goode, W. E., Gratch, S., Kincaid, J. F., Spell, A., and Stroupe, J. D., J. Am. Chem. Soc., 80, 1768 (1958).

38. Stroupe, J. D., and Hughes, R. E., J. Am. Chem. Soc., 80, 2341 (1958).

39. Katchalsky, A., and Eisenberg, H., J. Polymer Sci., 6, 145 (1951).

40. Organic Syntheses, Col. Vol. II, p. 165, John Wiley and Sons, Inc., New York (1943).

41. Baxendale, J. H., Bywater, S., and Evans, M., J. Polymer Sci., 1, 237 (1946).

42. Hwa, J., J. Am. Chem. Soc., 82, 0000 (1960).

43. Coleman, B. D., J. Polymer Sci., 31, 155 (1958).

44. Burleigh, P. H., J. Am. Chem. Soc., 82, 749 (1960).

45. Fox, T. G., Goode, W. E., Gratch, S., Huggett, C. M., Kincaid, J. F., Spell, A., and Stroupe, J. D., J. Polymer Sci., 31, 173 (1958).

46. Huggins, M. L., J. Am. Chem. Soc., 66, 1991 (1944).

BIOGRAPHICAL NOTES

W. Lamar Miller was born January 20, 1935, in Ackerman, Mississippi. He received all of his early training in the public schools of that state. He graduated from Clinton High School, Clinton, Mississippi, in June, 1953.

In June, 1952, he entered Mississippi College, from which he received the Bachelor of Science degree in June, 1955.

He entered the Graduate School of the University of Florida in September, 1955, where he was employed as a research assistant for some time. He received the degree Master of Science in Chemistry in February, 1958.

He held the Chemstrand Fellowship for Research in High Polymers during the academic year 1959-1960 and prior to that had been appointed a teaching assistant in the Department of Chemistry for the same period.

He is a member of the American Chemical Society and Alpha Chi Sigma, the Chemical Professional Fraternity.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

January 28, 1961

A H Gropp
Dean, College of Arts and Sciences

Dean, Graduate School

SUPERVISORY COMMITTEE:

G. B. Butler
Chairman

W S Brey

W. T. Lippincott

A H Gropp

UNIVERSITY OF FLORIDA
3 1262 08553 7974